

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of
Kan FUJIHARA et al.
Serial No: 10/667,184
Filed: September 19, 2003
For: POLYIMIDE FILM AND LAMINATE
HAVING METAL LAYER AND
SAME

Art Unit: 1711
Examiner: Thao T. Tran
Confirmation No. 7184

DECLARATION OF KAN FUJIHARA PURSUANT TO 37 C.F.R. 1.132

1. I, Kan Fujihara, am a named inventor of the present application. I am currently employed as an Assistant Manager, Electronic Materials R&D Group, Electrical & Electronic Materials Division by assignee Kaneka Corporation. I graduated from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Osaka, Japan, in 1995. I received the degree of Master of Chemistry from Osaka University Graduate School, Osaka, Japan in 1997 and the degree of Doctor of Chemistry from Osaka University Graduate School, Osaka, Japan in 2000. I have been employed by Kaneka Corporation for 5 years. I have been engaged in the development of polyimide film since 2000.

2. All statements made herein based on my own knowledge are true and all statements made on information and belief are believed to be true.

3. I conducted the experiments that are described in Exhibit A, entitled "Data from Comparative Experiment."

4. The experiments described in Exhibit A were performed by me (or under my supervision) between April 25, 2005 and July 13, 2005 at the Kaneka Corporation located at Shiga, Japan.

I declare under penalty of perjury under the laws the United States that the foregoing is true and correct. I acknowledge that willful false statements and the like are punishable by fine or imprisonment, or both and may jeopardize the validity of the application or any patent issuing thereon.

Appl. No. 10/667,184
Reply to Office Action of March 2, 2005

PATENT
Customer No. 26021

Dated this 28th day of July, 2005 at Osaka, Japan

Han Fujihara
signature of declarant

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Data from Comparative Experiment

Comparative Experiment 1

A polyimide film (thickness = 25 μm) was fabricated in accordance with Akahori, example 1.

Comparative Experiment 2

A polyimide film (thickness = 25 μm) was fabricated in accordance with Akahori, example 2.

Comparative Experiment 3

A polyimide film (thickness = 25 μm) was fabricated in accordance with Akahori, example 4.

Comparative Experiment 4

A polyimide film (thickness = 25 μm) was fabricated in accordance with Akahori, example 6.

Comparative Experiment 5

A polyimide film (thickness = 25 μm) was fabricated in accordance with Akahori, example 9.

Comparative Experiment 6

A polyimide film (thickness = 25 μm) was fabricated in accordance with Akahori, example 12.



Measurement of Dynamic Viscoelasticity Behavior

Dynamic viscoelasticity behavior was measured in the same manner as the examples in the present application, except that the measurement temperature profile was changed to 20°C to 500°C (Temperature rising rate = 3°C/minute).

The $\tan\delta$ peak temperature and the $\tan\delta$ value at 300°C were also obtained in the same manner as the examples in the present application.

Measurement of Alkali Etching Speed

Alkali etching speed was measured in the same manner as the examples in the present application.

Results

Results of the comparative experiment are shown in Table 1.

Table 1

Comparative Experiment	Temp. of $\tan\delta$ peak (°C)	$\tan\delta$ (300°C)	Alkali Etching Speed ($\mu\text{m}/\text{one side}/\text{min}$)
1	443	0.0094	-0.18
2	446	0.0004	-0.40
3	416	0.0060	-0.19
4	417	0.0050	-0.97
5	424	0.0005	-0.33
6	450 \leq	0.0001	-0.75

The $\tan\delta$ peak temperature was out of the 310 to 410°C range

in all of comparative experiments 1 to 6. None of the results met the polyimide film conditions given in claim 1.

The alkali etching speed was 0.1 $\mu\text{m}/\text{minute}$ or lower in all of comparative experiments 1 to 6. None of the results met the polyimide film conditions given in claim 11.

Person Who Conducted Comparative Experiments

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(14) DEGRADATION OF THE POLYIMIDE/COPPER INTERFACE

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ABSTRACT

A comparative investigation of polyimide/Cu interface degradation has been carried out for ultrathin photosensitive, non-photosensitive, and preimidized polyimide precursor films cured while in contact with a Cu substrate. The role of curing byproducts and environmental conditions on interface degradation has been elucidated by means of X-ray photoelectron spectroscopy. Immediately after curing, we observed some oxidation of the Cu in contact with non-photosensitive and photosensitive polyimide overlayers. On the other hand, only negligible oxidation was observed for the preimidized polyimide/Cu interface. Experiments in which samples were stored in vacuum, air and a humidity chamber show a dependence of the oxidation kinetics on air/moisture exposure. Preimidized and photosensitive polyimide/Cu interfaces, stored in air, became more extensively oxidized with time relative to identical samples stored in vacuum. Moreover, all three polyimide/Cu interfaces exhibited significantly more oxidation after 3 days in a humidity chamber than after 19 days of storage in air. Taken together, these data clearly demonstrate that absorbed water and its interaction with curing byproducts are key factors in the extent of Cu oxidation at the interface.

INTRODUCTION

Excellent thermal stability, adherence, and favorable dielectric properties have resulted in the widespread use of polyimide for microelectronics applications. Polyimide has been used as an interlevel dielectric [1] and a final passivant [2] for multilevel metal transistors. More recently, polyimide has been used as a dielectric in multilayer thin film interconnect structures such as multi-chip modules [3,4]. Most of these applications involve a substantial number of metal-polyimide interfaces. Therefore the nature of interfacial bonding between the two materials is a key parameter in the overall reliability of the structures. Consequently, a number of studies have been performed in which the chemistry of interface formation for metals evaporated onto cured polyimide films in an ultrahigh vacuum system has been investigated using X-ray photoelectron spectroscopy [5-7]. The first observation of Cu oxidation at the inverted polyimide on Cu interface was recently reported by Chambers and Chakravorty [8]. Most of these studies have focused on a nonphotosensitive, PMDA-ODA precursor type of polyimide. Similar information is lacking for the other types of polyimide used for microelectronics applications, such as the photosensitive precursor-based and preimidized versions. Due to their significantly different precursor composition and curing chemistry, different interfacial interactions are expected. Therefore, our goal in the present work has been to examine polyimide/Cu interfaces for these three different types of polyimide and to bring out any systematics that may exist between curing chemistry, environmental conditions and interface degradation.

EXPERIMENTAL

We selected Du Pont Pyralin PI-2525 as a representative of the nonphotosensitive PMDA-ODA precursor class of polyimides. Selectiplux HTR3 of EM Industries, Inc. and Pyralin LTP PI-2590D of Du Pont company were selected as a photosensitive and a preimidized polyimide, respectively. Polyimide solutions were diluted and spun at 6000 rpm onto 1000 Å of evaporated Cu on SiO₂/Si wafers. The oxide present on the metal films was stripped by immersion in 1.2 N H₂SO₄ followed by prolonged rinsing in de-ionized water prior to spin coating. The thin polyimide films were then cured by heating to 380 °C over 2 1/4 hours and holding at 380 °C for 3/4 hour. Upon cooling to room temperature in the oven, the samples were divided into three groups, each containing the three kinds of polyimide. The first group was stored in vacuum, the second group was stored in air at room temperature and the third group was aged in a controlled humidity chamber at 85 °C and 85% relative humidity. Cu 2p X-ray photoelectron spectra were obtained every few days for a period of three weeks for each sample. The spectrometer employed was a Surface Science Instruments Model 301 with a focussed, monochromatic AlKα X-ray source. All spectra were obtained with an analyzer pass energy of 150 eV, an X-ray beam diameter of 1000 μ, and a collection angle of 90° with respect to the surface.

RESULTS AND DISCUSSION

In order to insure that the polyimide films were continuous, scanning Auger microprobe and scanning electron microscopy analysis was done. Characterization of several regions of each sample showed that the films were indeed continuous and free of voids. Point spectra exhibited C, N and O KLL peaks yielding atomic concentrations in good agreement with those obtained by XPS. The Cu LMM peak was clearly present, but significantly attenuated, again indicating continuous coverage of the polymer overlayers. The continuity of the films prevents direct contact of oxygen with the Cu substrate so that any observed oxidation will be caused either directly or indirectly by the polyimide rather than by oxygen.

In figure 1 we show Cu 2p_{3/2} spectra for the three Cu surfaces with overlayers of preimidized, nonphotosensitive and photosensitive polyimide stored in air as a function of time. Also included at the top of each column is a Cu 2p_{3/2} reference spectrum obtained for a Cu surface, freshly stripped of its surface oxide and without any polyimide overlayer. The absence of a shoulder to higher binding energy establishes complete removal of the metal oxide in the starting metal surfaces. Spectra for the three polyimide/Cu interfaces stored in the humidity chamber are shown at the bottom. The first set of spectra (corresponding to day 1) were recorded within a few hours of the samples being removed from the oven. Based on attenuation of the total Cu 2p_{3/2} peak intensity relative to that for a clean Cu surface, we estimate that the film thicknesses were 30, 45, and 65 Å for preimidized, nonphotosensitive, and photosensitive polyimide samples, respectively.

Immediately after curing, there was evidence of partial oxidation of Cu at the interface by non-photosensitive and photosensitive polyimide overlayers. The amount of oxide at the preimidized polyimide/Cu interface was negligible. A shoulder on the Cu 2p_{3/2} peak, shifted approximately 2 eV to higher binding energy, shows that some of the Cu at the interface had been oxidized to a probable combination of +1 and +2 oxidation states within one hour of being removed from the oven. Exposure to air increased the extent of oxidation of Cu at the interface for all three polyimides.

Although it appears that the extent of oxidation was highest at any given time for the Cu surface supporting the photosensitive polyimide film, this observation may be due to the higher polyimide film thickness for this sample (65 Å) compared to the other two (45 and 30 Å). In this case, the ratio of oxidized to elemental Cu peak intensity is artificially increased because of preferential attenuation (by the thicker polyimide film) of photoelectrons originating below the interfacial region. Exposure of samples to an increased level of humidity accelerated the rate of Cu oxidation for all three kinds of polyimide. After 3 days of aging at 85 °C and 85% relative humidity conditions, all three Cu interfaces were considerably more oxidized than after 19 days of air exposure.

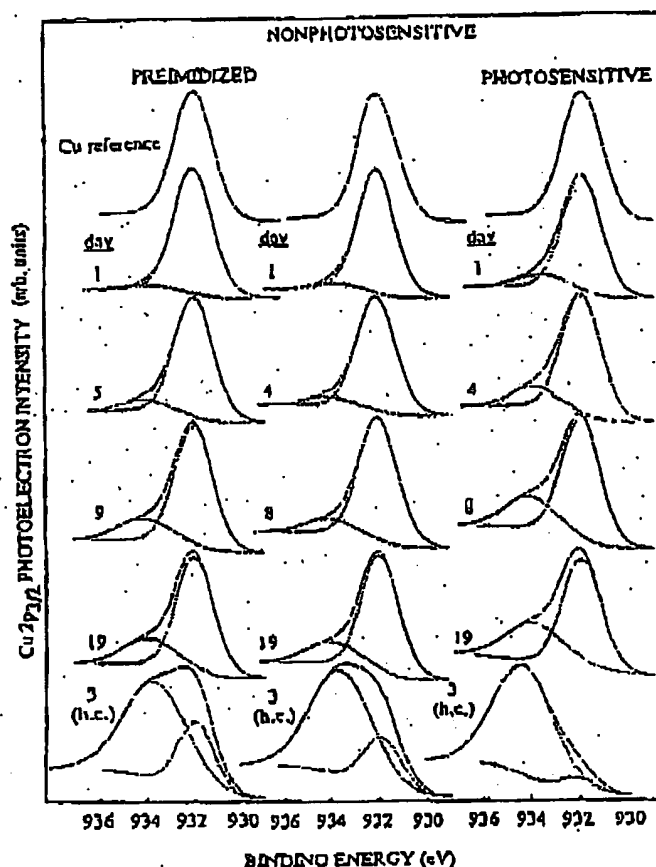


Figure 1. Cu $2p_{3/2}$ spectra for three Cu surfaces with overlayers of preimide, nonphotosensitive and photosensitive polyimide stored in air as a function of time. Decomposition of the spectra into contributions from the elemental and the oxidized state is indicated with Gaussians. The last set of spectra labeled h.c. were recorded for samples aged in a humidity chamber at 85 °C and 85% relative humidity. Also included at the top of each column is a Cu $2p_{3/2}$ reference spectrum for a bare Cu surface.

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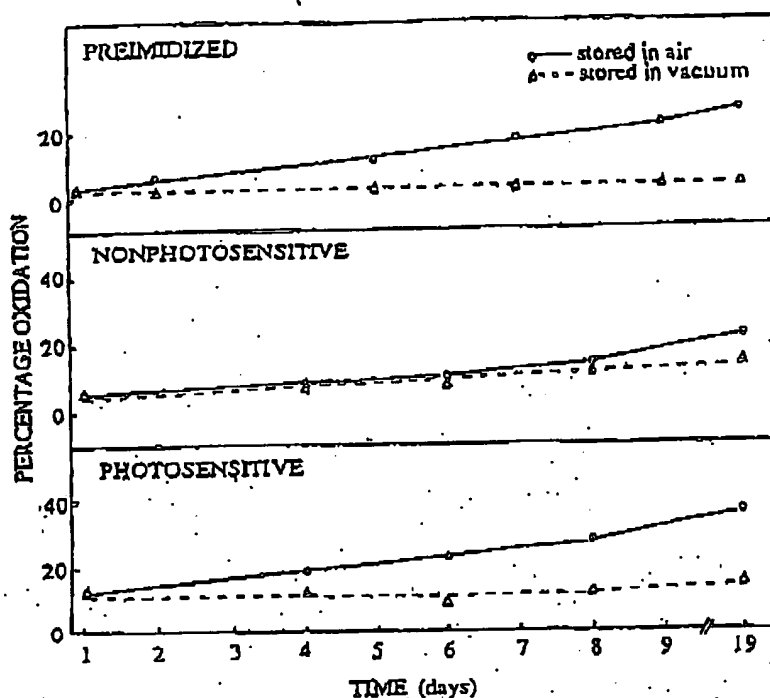


Figure 2. Percentage oxidation of the preimidized, nonphotosensitive and photosensitive polyimide samples as a function of storage in air and vacuum. We define percentage oxidation as the ratio of Cu $2p_{3/2}$ peak intensity associated with the oxidized state to that for elemental Cu.

In figure 2 we plot the percentage oxidation of Cu at the interface for samples exposed to air and those stored in vacuum. In the case of preimidized and photosensitive polyimides, storing the samples in vacuum resulted in a significantly lower rate of oxidation of the interfacial Cu than did storing similar samples in air. Cu in contact with the preimidized polyimide overlayer undergoes only negligible oxidation even after 9 days of storage in a vacuum environment. The photosensitive polyimide/Cu interface does not oxidize beyond the stage associated with curing, even after several days of vacuum storage. In contrast, the samples stored in air showed a monotonic increase in the percentage oxidation as a function of storage time. The amount of interfacial Cu that was oxidized in the air-stored samples increased by factors of 12 and 3 for the preimidized and photosensitive polyimides, respectively, over the 19 day period. In contrast, the nonphotosensitive polyimide/Cu interface showed nearly the same rate of oxidation in both air and vacuum.

The different oxidation behavior described above suggests that Cu/polyimide interface degradation depends on curing chemistry in the

precursor overlayer. The three polyimide samples included in the present study differ significantly in their curing chemistry. The preimidized version is imidized at the precursor level. Therefore, a high-temperature curing step involves primarily desorption of the solvent [9]. The absence of any significant oxidation of Cu at the interface after curing this polyimide suggests that neither the polymer nor the solvent system (80/20 N-methyl-2-pyrrolidone/aromatic hydrocarbon [9]) interacts chemically with the Cu surface at elevated temperatures. The hygroscopic nature of polyimide films and consequent degradation of their dielectric properties in humid environments are well established [10]. It appears from the different rates of oxidation in air and in vacuum that the uptake of water in the hygroscopic polyimide film, brought about by air exposure is the driving force in the oxidation of the buried Cu surface.

The nonphotosensitive polyimide employed in the present study undergoes an imidization reaction of the polyamic acid precursor at elevated temperatures. The initial cure of the polyamic acid precursor (poly (4,4'-oxydiphenylpyromellitic acid)) is suggested to proceed through transimidization rather than cyclization. Cyclization of some of the trans imide is achieved in the subsequent elevated-temperature annealing step [11]. The imidization reaction is accompanied by formation of water. Partial oxidation of the Cu surface in contact with the polyimide overlayers immediately after curing the polyimide film suggests a reactive interaction between the interfacial Cu atoms and water that is present from the imidization reactions and/or absorbed during air exposure. However, the near constancy in the rate of oxidation in air and vacuum strongly suggests that water produced in the imidization reaction is sufficient to drive the oxidation, and that absorbed water plays only a minor role.

Photosensitive polyimide precursors generally consist of polyamic acid esters. The ester group, such as oxyethylmethacrylate [12], forms an insoluble crosslinked chemical intermediate upon irradiation with UV light. High temperature annealing causes imidization and polyimide ring closure via cleavage of the ester groups. The crosslinked photosensitive groups are depolymerized and volatilized. In the case of the polyimide precursor which contains an oxyethylmethacrylate photoreactive group, the curing by-products are expected to be mono- and poly-hydroxyethylmethacrylate [12]. Significant oxidation of the Cu surface immediately after curing of this polyimide is suggestive of a chemical interaction involving curing byproducts and Cu. However, it appears that absorbed water is key to sustaining the oxidation process, inasmuch as the reaction comes to a halt when the sample is stored in vacuum.

Enhancement of Cu surface oxidation upon exposure to a humid environment for all three polyimide samples lends considerable support to a moisture-induced oxidation mechanism. This reaction may be brought about by an ionic-contaminant-catalyzed corrosive action [8]. Cu/Pent Kapton H type polyimide samples, metallized with evaporated Cu, show increased polymer-metal intermixing but apparently no oxide formation at the polyimide/Cu interface [13]. Our observation of substantial oxidation of Cu at the polyimide/Cu interface after a three-day exposure in a 85/85 humidity chamber is indicative of significant chemical activity. Moisture absorption by the cured polyimide film accelerates the interface reaction started during the curing of the precursor groups. The O1s spectra for these polyimide/Cu interfaces underwent significant changes as oxidation of the Cu surface occurred and may yield further insight into the details of interfacial degradation. We are currently analyzing these spectra and will report on them at a later time.

CONCLUSION

The process of curing ultrathin films of photosensitive and nonphotosensitive polyimide over Cu causes significant oxidation of the Cu surface. In contrast, negligible oxidation is observed for a preimidized polyimide sample. The oxidation kinetics after curing show a strong dependence on moisture absorption from air and a highly humid environment. The observed oxidation behavior appears to support a mechanism whereby moisture absorbed by the cured polyimide film accelerates the interface reaction started during curing of the precursor groups.

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